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**(19) (CA) APPLICATION FOR CANADIAN PATENT (12)**

(54) Aqueous Polyurethane Dispersion

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Notice: This application is as filed and may therefore contain an  
incomplete specification.

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Aqueous Polyurethane Dispersion***Abstract of the disclosure:***

An aqueous dispersion containing a polyurethane and from 5 to 60 wt%, based on the polyurethane, of a polymeric adhesion enhancer, the polyurethane being essentially built up of

- 5 (a) an organic polyisocyanate,
- (b) a dihydroxyl compound having a molecular weight exceeding 500 and ranging up to 5000 g/mol and not containing any anionic groups or groups capable of conversion to anionic groups,
- 10 (c) a di- or mono-hydroxyl compound containing carboxylic acid groups or carboxylate groups,
- 15 (d) optionally a further compound different from (c) and containing one or two isocyanate-reactive functional groups and at least one anionic group or a group capable of conversion to an anionic group,
- (e) optionally a compound different from (c) and (d) and having two isocyanate-reactive functional groups and a molecular weight of from 60 to 500 g/mol,

20 and the polyurethane or its prepolymer is prepared in a water-miscible solvent boiling below 100°C and, following the addition of the polymeric adhesion enhancer, is dispersed in water and, in the case of the prepolymer, the conversion of the latter to the polyurethane is carried out.

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## Aqueous Polyurethane Dispersion

The invention relates to an aqueous dispersion containing a polyurethane and from 5 to 60 wt%, based on the polyurethane, of a polymeric adhesion enhancer, the polyurethane being essentially built up of

- s (a) an organic polyisocyanate,
- 10 (b) a dihydroxyl compound having a molecular weight exceeding 500 and ranging up to 5000 g/mol and not containing any anionic groups or groups capable of conversion to anionic groups,
- 15 (c) a di- or mono-hydroxyl compound containing at least one anionic group or a group capable of conversion to an anionic group,
- (d) optionally a further compound different from (c) and containing one or two isocyanate-reactive functional groups and at least one anionic group or a group capable of conversion to an anionic group,
- 20 (e) optionally a compound having at least two isocyanate-reactive functional groups and a molecular weight of from 60 to 500 g/mol and not containing any anionic groups or groups capable of conversion to anionic groups,

and the polyurethane or its prepolymer is prepared in a water-miscible solvent boiling below 100°C and, following the addition of the polymeric adhesion enhancer, is dispersed in water and, in the case of the prepolymer, the conversion 25 of the latter to the polyurethane is carried out.

German Patent Application 4,024,567 and DE-A 3,903,538 disclose emulsifier-free dispersions for use as adhesives, which contain a polyurethane and other polymers, for example a phenol-formaldehyde resin, which enhance the adhesive 30 characteristics. In the process described in DE-A 3,903,538, the polyurethane is prepared in a low-boiling water-miscible solvent, after which the polymeric adhesion enhancer is added and the resulting mixture is then dispersed in water.

This procedure produces stable aqueous dispersions in which the added polymeric 35 adhesion enhancer is presumably located inside the dispersed particles, where it is surrounded by a stabilizing layer of polyurethane. A particularly marked positive

feature of such dispersions, when used as adhesives, is their good initial adhesive strength.

A negative feature of these dispersions, however, is that they are still too viscous.

5 Such adhesives must in general be applied in the form of highly concentrated dispersions, preferably of low viscosity. At the same time, the particles contained therein must be fine to ensure that the dispersion has a high shear strength.

It is thus an object of the invention to provide dispersions having good adhesion

10 properties and minimum viscosity.

Accordingly, we have found the dispersions defined above and their use as adhesives.

15 Preferred embodiments of the invention are disclosed in the sub-claims.

The emulsion-free dispersions of the invention contain a polyurethane and from 5 to 60 wt%, based on the polyurethane, of a polymeric adhesion enhancer.

20 The polyurethane is substantially, and preferably exclusively, composed of the constituents (a) to (e). The isocyanate-reactive functional groups are hydroxyl groups or primary or secondary amino groups.

25 Particularly suitable polyisocyanates (a) are aliphatic, cycloaliphatic, and aromatic diisocyanates. The polyisocyanates preferably used have the general formula  $X(NCO)_2$ , where X stands for an aliphatic hydrocarbon radical having from 4 to 12 carbon atoms, a cycloaliphatic hydrocarbon radical having from 6 to 15 carbon atoms, or an aromatic hydrocarbon radical having from 6 to 15 carbon atoms.

30 Examples of suitable aliphatic, cycloaliphatic, and aromatic diisocyanates are 1,4-butane diisocyanate, 1,6-hexane diisocyanate, 2,2,4- and 2,4,4-trimethylhexamethylene diisocyanates, cyclohexane diisocyanate, methylcyclohexane diisocyanate, isophorone diisocyanate, 4,4'-diisocyanatodiphenylmethane, 4,4'-diisocyanatodicyclohexylmethane, and 2,4- and 2,6-toluene diisocyanates.

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Mixtures of these diisocyanates may be used, if desired. Particularly suitable mixtures are those of aliphatic or cycloaliphatic diisocyanates with aromatic diisocyanates in a molar ratio of from 1:4 to 5:1.

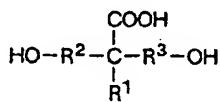
40 The diisocyanates may be supplemented by minor quantities of monoisocyanates,

if desired, to regulate the molecular weight.

Suitable dihydroxyl compounds (b) having a molecular weight exceeding 500 and ranging up to 5000 g/mol are the well-known polyesters, polyethers, polythioethers, polylactones, polyacetals, polycarbonates, and polyesteramides containing two hydroxyl groups. The preferred dihydroxyl compounds are those having molecular weights between 750 and 3000. Mixtures of these dihydroxyl compounds can, of course, be used if desired.

10 Suitable components (c) are aliphatic, cycloaliphatic, and aromatic mono- or dihydroxycarboxylic acids. Use is preferably made of dihydroxy-alkylcarboxylic acids, and more preferably of such acids having from 3 to 10 carbon atoms, such as are described in US-A 3,412,054. Particularly preferred compounds are those of the general formula

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20 in which R<sup>1</sup> denotes a hydrogen atom or an alkyl radical of from 1 to 4 carbon atoms, and R<sup>2</sup> and R<sup>3</sup> stand for a C<sub>1</sub>-C<sub>4</sub> alkylene group. An example of such a compound is 2,2-dimethylolpropionic acid.

25 The optional constituent (d) may be a compound different from (c) and containing one or two isocyanate-reactive amino groups and at least one anionic group or a group capable of conversion to an anionic group. The groups which are capable of conversion to anionic groups are usually carboxylic acid groups or sulfonic acid groups. Worthy of mention are aminocarboxylic acids and aminosulfonic acids, for example lysine, -alanine, N-(2-aminoethyl)-2-aminoethanesulfonic acid, and the adducts of aliphatic diprimary diamines on  $\alpha$ -olefinic carboxylic acids as described 30 in DE-A 2,034,479, eg, the adduct of ethylenediamine on acrylic acid.

35 Both of the components (c) and (d) contain ionic groups, or groups which are capable of conversion to ionic groups, to ensure that the polyurethane is dispersible in water.

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In order to convert potentially anionic groups, eg, carboxylic acid groups or sulfonic acid groups, to ionic groups, use may be made of inorganic and/or organic bases such as sodium hydroxide, potassium hydroxide, potassium carbonate, sodium bicarbonate, ammonia, or primary, secondary, and, in particular, tertiary 40 amines, eg, triethylamine or dimethylaminopropanol.

The neutralization of the potentially anionic groups may be effected before, during, but preferably after, the isocyanate polyaddition reaction.

If desired, additional emulsifying constituents may also be used, for example <sup>15</sup> monohydric polyether alcohols having a molecular weight of from 500 to 10,000 g/mol and preferably from 1,000 to 5,000 g/mol. Monohydric polyether alcohols can be obtained by alkoxylation of monohydric starting molecules such as methanol, ethanol, or *n*-butanol, the alkoxylating agent being ethylene oxide or a mixture of ethylene oxide with some other alkylene oxide, especially propylene oxide. When such mixtures are used, they preferably contain at least 40 mol%, and more preferably at least 65 mol%, of ethylene oxide.

However, the addition of such nonionic emulsifiers is not generally necessary due to the presence of constituent (c) and, optionally, constituent (d).

<sup>15</sup> The constituent (e) is essentially a compound having two hydroxyl groups, or two amino groups, or one hydroxyl group and one amino group. Examples of suitable compounds are dihydroxyl compounds such as 1,3-propanediol, 1,4-butanediol, diamines such as ethylene diamine, hexamethylene diamine, piperazine, 2,5-dimethylpiperazine, 1-amino-3-aminomethyl-3,5,5-trimethylcyclohexane (isophorone diamine), 4,4'-diaminodicyclohexylmethane, 2,4-diaminocyclohexane, 1,2-diaminopropane, hydrazine, and amino alcohols such as ethanolamine, isopropanolamine, methylethanolamine, and aminoethoxyethanol. If desired, compounds (e) having more than two isocyanate-reactive groups can be used.

<sup>25</sup> Preferably, the weights of the components (a) to (e) are such that the total number of isocyanate-reactive functional groups, generally hydroxyl groups or amino groups, represents from 0.9 to 1.1 and more preferably from 0.95 to 1.05 gram equivalents per gram equivalent of isocyanate.

<sup>30</sup> The most preferred situation is when the number of isocyanate-reactive functional groups is equal to that of the isocyanate groups.

<sup>35</sup> The proportions of the individual components, based on one gram equivalent of isocyanate, are preferably as follows:

component (b) from 0.15 to 0.8 and more preferably from 0.3 to 0.6 gram equivalents,

<sup>40</sup> component (c) from 0.03 to 0.4 and more preferably from 0.05 to 0.4 gram

equivalents,

component (d) from 0 to 0.4 and more preferably from 0 to 0.3 gram equivalents,

component (e) from 0 to 0.8 and more preferably from 0 to 0.6 gram equivalents.

In order to prepare the polyurethane, the constituents (a) to (e) are reacted in known manner in a water-miscible low-boiling organic solvent, as described, for example, in DE-A 3,437,918.

Examples of particularly recommendable solvents are tetrahydrofuran, methylethyl ketone, *N*-methylpyrrolidone, are especially acetone.

The reaction temperature is preferably from 50° to 100°C.

The diisocyanate reaction can be accelerated by including conventional and well-known catalysts such as dibutyltin dilaurate, tin(II) octoate, or 1,4-diazabicyclo-[2.2.2]octane.

The resulting polyurethane, which is substantially free from isocyanate groups, is dispersed in water after the addition of the polymeric adhesion enhancer, and the organic solvent is then removed, by distillation, to the desired extent, usually completely.

Alternatively, the polyurethane may be prepared by first producing a polyurethane prepolymer in the water-miscible low-boiling organic solvent. To this end, at least the constituents (a) and (b) and a portion of (c) are interreacted. After the addition of the polymeric adhesion enhancer, the resulting polyurethane prepolymer, which still contains isocyanate groups, is dispersed in water. The reaction of the prepolymer is then continued, in particular, with the remaining constituents. The organic solvent can then be removed in the manner described above.

The polymeric adhesion enhancer can be one of a number of different polycondensates, polymers produced by free-radical polymerization, or poly-adducts.

The polymeric adhesion enhancer is preferably a phenol-formaldehyde condensation resin preferably having a molecular weight (weight average  $\bar{M}_w$ ) of from 500 to 2000 and a softening point ranging from 80° to 130°C. Particularly preferred

phenol-formaldehyde condensation resins are novolaks, as may be obtained by acid-catalyzed reaction of phenols, particularly phenol or phenol substituted by  $C_1$ - $C_{10}$  alkyl groups, with formaldehyde. More particularly, the reaction is carried out using from 1.05 to 1.3 mol of phenols per mole of formaldehyde.

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Also particularly suitable are epoxy resins, preferably the reaction products of epoxides such as epichlorohydrin with bisphenol A, those being particularly preferred which have a molecular weight (weight average  $M_w$ ) of from 500 to 5000 and a softening point ranging from 80° to 130°C.

10

Other suitable polymeric adhesion enhancers are poly(vinyl acetate), poly(vinyl chloride), poly(methyl methacrylate), polyamides, polyethers, polyesters, polyetherdiols, polyesterdiols, polyurethanes, especially polyurethanes free from salt groups, and phenacrylates.

15

Preferred poly(vinyl acetate)s are homopolymers of vinyl acetate. Also useful are the copolymers thereof containing up to 10 wt% of comonomers such as vinyl laurate, vinyl stearate, or, preferably, esters of (meth)acrylic acid or fumaric acid or maleic acid with  $C_1$ - $C_8$  alkanols such as methanol, *n*-butanol, or 2-ethylhexanol.

20

The polymers usually have a *K*-value, as measured at 25°C in cyclohexanone as specified in DIN 53,726, of from 45 to 60. By poly(vinyl chloride) we generally mean homopolymers of vinyl chloride or copolymers thereof containing up to 10 wt% of comonomer such as ethylene or vinyl acetate. Their *K*-value (25°C, cyclohexanone, DIN 53,726) should be between 45 and 55. The poly(methyl

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methacrylate)s used by the person skilled in the art will normally be homopolymers of methyl methacrylate or copolymers thereof containing up to 10 wt%, based on the weight of the copolymer, of vinyl acetate, an ester of acrylic acid with a  $C_1$ - $C_8$  alkanol, or an ester of methacrylic acid with a  $C_2$ - $C_8$  alkanol. Their melt flow index MFI, determined as specified in DIN 53,735 (230°C/3.8 kg) is generally between

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0.1 and 3.0. The synthesis of such polymers is generally carried out by free-radical polymerization of the ethylenically unsaturated monomers at a temperature between 30° and 150°C in substance, in solution, or in emulsion, followed by drying. Such polymers are well known, eg, from Houben-Weyl, Methoden der Organischen Chemie, Vol. E20, 1987, pp. 1115-1125, 1041-1062, and 1141-

35 1174.

Suitable polyamides have a *K*-value of from 65 to 80, determined in sulfuric acid at 25°C as specified in DIN 53,727. They are usually polymers derived from lactams having from 7 to 13 ring units such as  $\epsilon$ -caprolactam,  $\epsilon$ -capryllactam, or  $\epsilon$ -

40 laurolactam, eg, polycaprolactam (PA6), or they may be polyamides produced by reacting dicarboxylic acids with diamines. Examples are poly(hexamethylene

adipamide) (PA66), poly(hexamethylene sebacamide) (PA610), and poly(hexamethylene dodecanamide) (PA612). Suitable dicarboxylic acids are, for example, alkanedioic acids containing from 4 to 12, and preferably from 6 to 10, carbon atoms, and phthalic acid, terephthalic acid, and isophthalic acid, as well as arbitrary mixtures of said acids. Examples of suitable diamines are alkanediamines having from 4 to 12, and preferably from 4 to 8, carbon atoms, and also *m*-xylylenediamine, *p*-xylylenediamine, their hydrogenated derivatives, bis(4-aminophenyl)methane, bis(4-aminocyclohexyl)methane, and bis(4-aminophenyl)propane-2,2, or mixtures thereof. Due to their good solubility properties, copolymers are preferred, for example a copolyamide of 30-40 wt% adipic acid, 15-20 wt% hexamethylenediamine, 30-35 wt%  $\epsilon$ -caprolactam, and 15-20 wt%  $\epsilon$ -aminocaproic acid. The manufacture of these well-known polymers is part of the specialized knowledge of the person skilled in the art, cf, eg, Römpf, *Chemielexikon*, 8th Edition, pp. 2861, 3058, and 3267, or EP-A 129,195 and EP-A 129,196.

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Polyetherdiols are known *per se*, for example from *Kunststoff-Handbuch* Vol.7 (1983) pp. 42 to 54. Examples are poly(ethylene oxide), poly(propylene oxide), and polytetrahydrofuran, or copolymers thereof containing two terminal hydroxyl groups. They are produced in known manner, generally by anionic polyaddition, cf, eg, N.G.Gaylord, *High Polymers*, Vol.13, New York 1963, Part I. Of minor significance are polyetherols grafted with ethylene oxide to increase reactivity. The polyetherdiols generally have a molecular weight of from 300 to 3000 corresponding to a *K*-value of from 25 to 60, as determined in DMF at 25°C as specified in DIN 53,726. Preferred molecular weights are between 800 and 2200 corresponding to *K*-values between 20 and 50.

The polyethers used are, eg, poly(ethylene oxide), poly(propylene oxide), and polytetrahydrofuran. The polyethers usually have a *K*-value in DMF at 25°C (DIN 53,726) of from 20 to 50. They are well known, cf, eg, *Encyclopedia of Polymer Science and Technology*, Vol.6, 1967, pp. 103 et seq, Vol.9, 1968, pp. 668 et seq, and Vol.13, 1970, pp. 670 et seq.

The preferred polyesters are monomer-free unsaturated polyester resins. These are known condensation polymers of polyvalent, preferably divalent, carboxylic acids and their esterifiable derivatives, especially their anhydrides, which are linked by an ester-like bond to polyhydric, preferably dihydric, alcohols and optionally contain additional radicals of monovalent carboxylic acids or of monohydric alcohols. Examples of the starting materials are as follows: maleic acid, fumaric acid, phthalic acid, isophthalic acid, terephthalic acid, maleic anhydride, phthalic anhydride, isophthalic anhydride, ethylene glycol, propylene glycol, 1,4-butanediol, and neopentyl glycol. Of minor significance for the present

invention are those resins which are prepared by co-condensation of bisphenol A, epichlorohydrin-bisphenol A condensates, and methacrylic acid. In this context, "monomer-free" means that these unsaturated polyester resins (UP resins) are not dissolved in a monomer, such as styrene, which could induce cross-linking. The products usually have a viscosity at 150°C of from 1000 to 6000 mPa·s and preferably from 2000 to 4000 mPa·s.

Suitable polyesterdiols are condensation polymers containing two terminal hydroxyl groups and derived from dicarboxylic acids such as adipic acid or isophthalic acid 10 condensed with diols such as 1,4-butanediol, 1,6-hexanediol, or neopentyl glycol.

The molecular weight range of the polyesterdiols used is generally from 300 to 5000. Preferred molecular weights are between 800 and 2500 corresponding to a K-value in DMF at 25°C (DIN 53,276) of from 30 to 55. These polymers and their 15 manufacture are generally known, cf *Kunststoff-Handbuch* Vol.7 (1983) pp. 54 to 62 and DE 1,268,842.

Salt group-free polyurethanes are known addition polymers based on polyetherdiols, polyesterdiols, isocyanates such as hexamethylene diisocyanate, 2,4- 20 diisocyanatodiphenylmethane, and possibly bifunctional or trifunctional chain extenders, which are prepared by conventional methods, cf *Kunststoff-Handbuch* Karl-Hanser-Verlag, Vol.7 (1966). The preferred condensates are those having a low molecular weight (K-value in DMF at 25°C as specified by DIN 53,726: from 25 to 60). Cross-linked polyurethanes are of minor importance.

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Phenacrylates are preferably made by the addition of bisphenol A glycidyl ether (meth)acrylates to terephthalic acid. It is also possible to use phenacrylates based on epoxidized novolaks. The K-values of these polymers generally range from 30 to 55 (determined in cyclohexane at 25°C as specified in DIN 53,726).

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The polymeric adhesion enhancer is added to the polyurethane or its prepolymer present in a water-miscible low-boiling organic solvent prior to dispersion thereof in water, ie, prior to the formation of the aqueous dispersion of the invention having an aqueous continuous phase. Basically, the resin can be added to the reaction 35 mixture of the starting components of the polyurethane at any desired time, but it is particularly advantageous not to add the resin until the prepolymer formation has reached an advanced stage and the NCO content of the prepolymer has reached a value of less than 1.5 wt%. Especially in the case of resins containing groups which are particularly reactive to isocyanates, such as the novolaks, the resins 40 should only be compounded with polyurethane resins having an NCO content near 0 wt%. The polymer may be added in substance or in the form of a solution.

Suitable solvents for the polymer are water (eg, in the case of phenol-formaldehyde resins) and, more particularly, again water-miscible low-boiling organic solvents.

9 The dispersion of the invention, as finally obtained following the dispersion of the mixture in water, the conversion of the polyurethane prepolymer to the polyurethane, if applicable, and the removal of the organic solvent by distillation, if necessary, preferably has a solids content of from 10 to 70 wt% and more preferably from 20 to 50 wt%.

10 The dispersions of the invention can be immediately used for making joints between widely varying substrates, for example wood, plastics, glass, and metal. To achieve special properties, it is possible to add auxiliaries to the dispersions, for example plasticizers, film formers, fillers, etc.

15 The dispersions have good adhesion properties and are particularly noteworthy for their initial adhesive strength, this being the result of their low viscosity. In general, the viscosity of a dispersion can be reduced by increasing the particle diameter without changing the solids content (O.Lorenz, G.Rose, *Colloid Polym. Sci.* 260 20 (1982) p. 1079). However, there is the risk of coagulation of larger dispersed particles, particularly when shearing forces are applied.

Surprisingly, the dispersions of the invention are even less viscous than dispersions containing particles of larger sizes.

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### Examples

The viscosities of the dispersions were measured at a shear rate of 100 s<sup>-1</sup> using a rotational rheometer comprising concentric cylinders (diameter of bob: 38.7 mm, 30 diameter of cup: 42.0 mm).

The particle size of the latex particles was determined indirectly via turbidity measurements, in which the turbidity of a dispersion having a solids content of 0.01 wt% was compared with distilled water at room temperature for a layer 35 thickness of 2.5cm.

$$LD = \frac{\text{Intensity}_{\text{dispersion}} \times 100}{\text{Intensity}_{\text{water}}}$$

In the following examples the symbols have the meanings given below:

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ADA = adipic acid

B14	=	1,4-butanediol
TDI	=	toluene diisocyanate
HDI	=	hexamethylene diisocyanate
PUD	=	Na salt of the Michael adduct of acrylic acid and ethylenediamine
DBTL	=	dibutyltin dilaurate
DMPA	=	dimethyolpropionic acid

## Comparative Example 1

10 TDI was added to a mixture of dehydrated polyesterol, acetone I and catalyst. After a reaction time of 1 hour at 65°C, HDI was added and the reaction continued for another 90 min. Following the addition of acetone II, the reaction mixture had an NCO content of 0.69 %.

15 Chain-extension was carried out at 50°C by the addition of PUD, this salt being in the form of a 40 % solution in water. After 5 min, the resin solution prepared from acetone III and Epikote 1001 was added and the mixture stirred for a further 5 min at 50°C. The mixture was then dispersed in water and the acetone distilled off.

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## Starting materials

	Molar amount [mmol]	Parts by weight	
		[g]	
Polyesterdiol ADA/B14 (OH number 45.2)	199	493	
25 TDI	148	25.8	
HDI	149	25.0	
DBTL		0.1	
Acetone I		133	
Acetone II		532	
30 Epikote 1001 (condensation product of bisphenol A and epichlorohydrin, M <sub>w</sub> ca 450-500)		240	
Acetone III		240	
PUD (40 % solution of salt)	95	41	
35 Deionized water		1200	

## Comparative Example 2

40 The TDI was added to the mixture of dehydrated polyesterol, 1,4-butanediol,

acetone I and catalyst. After a reaction time of 1 hour at 65°C, the HDI was added and the reaction continued for another 90 min. Following the addition of acetone II, the reaction mixture had an NCO content of 0.63 %.

5 Chain-extension was carried out at 50°C by the addition of PUD, this salt being in the form of a 40 % solution in water. After 5 min, the resin solution prepared from acetone III and a polyesterol was added and the mixture stirred for a further 5 min at 50°C. The mixture was then dispersed in water and the acetone distilled off.

10

### Starting materials

	Molar amount [mmol]	Parts by weight [g]
Polyesterdiol ADA/B14 (OH number 45.0)	193	482
15 1,4-butanediol	58	5.2
TDI	169	29.4
HDI	169	28.3
Acetone I		133
Acetone II		533
20 Polyesterdiol ADA/B14 (OH number = 45.0)		240
Acetone III		240
PUD (40 % solution of salt)	86	37.5
Deionized water		1200

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### Comparative Example 3

The TDI was added to the mixture of dehydrated poly(tetramethylene oxide), 1,4-  
30 butanediol, acetone I and catalyst. After a reaction time of 1 hour at 65°C, the HDI was added and the reaction continued for another 90 min. Following the addition of acetone II, the reaction mixture had an NCO content of 0.70 %.

Chain-extension was carried out at 50°C by the addition of PUD, this salt being in  
35 the form of a 40 % solution in water. After 5 min, the resin solution prepared from acetone III and Epikote 1007 was added and the mixture stirred for a further 5 min at 50°C. The mixture was then dispersed in water and the acetone distilled off.

## Starting materials

	Molar amount [mmol]	Parts by weight [g]
5 Poly(tetramethylene oxide) (OH-number 45.0)	213	435
1,4-Butanediol	213	19.2
TDI	260	45.3
HDI	260	43.8
Acetone I		132
10 Acetone II		532
Epikote 1007 (condensation polymer of bisphenol A and epichlorohydrin, $M_w$ ca 1550-2000)		240
Acetone III		240
15 PUD (40 % solution of salt)	94	41
Deionized water		1200

## Example 1

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The TDI was added to the mixture of dehydrated polyesterol, DMPA, acetone I and catalyst. After a reaction time of 1 hour at 65°C, the HDI was added and the reaction continued for another 90 min. Following the addition of acetone II, the reaction mixture had an NCO content of 0.65 %.

25

Chain-extension was carried out at 50°C by the addition of PUD, this salt being in the form of a 40 % solution in water. After 5 min, the resin solution prepared from acetone III and Epikote 1007 was added and the mixture stirred for a further 5 min at 50°C. The mixture was then dispersed in water and the acetone distilled off.

30

## Starting materials

	Molar amount [mmol]	Parts by weight [g]
35 Polyesterdiol ADA/B14 (OH number = 45.2)	194	481
DMPA	56	7.4
TDI	164	28.6
HDI	167	28.1
DBTL		0.1
40 Acetone I		133

Acetone II		533
PUD (40 % solution of salt)	84	36.8
Aceton III		240
Epikote 1007 (condensation product of bisphenol A and epichlorohydrin, $M_w$ ca 1550-2000)		240
Deionized water		1200

## 10 Example 2

## Procedure:

15 The TDI was added to the mixture of dehydrated polyesterol, 1,4-butanediol,  
DMPA, acetone I and catalyst. After a reaction time of 1 hour at 65°C, the HDI was  
added and the reaction continued for another 90 min. Following the addition of  
acetone II, the reaction mixture had an NCO content of 0.60 %. The reaction  
mixture was cooled to 30°C and then mixed with the resin solution prepared from  
Lupraphen VP 9186 and acetone III. The mixture was then neutralized with 30 %  
20 caustic soda solution and dispersed in deionized water. The acetone was then  
distilled off.

## Starting materials

	Molar amount	Parts by weight	
		[mmol]	[g]
Polyesterdiol ADA/B14 (OH number = 45.0)	166		414
1,4-Butanediol	50		4.5
DMPA	250		3.5
30 TDI	273		47.6
HDI	273		45.9
DBTL			0.1
Acetone I			134
Acetone II			534
35 Polyester resin:			
Lupraphen VP 9186			
Polyesterdiol ADA/B14 (OH number = 47)			240
Aceton III			240
NaOH solution (30 %)	187		25.0
Deionized water			1200

Example 3

The TDI was added to the mixture of dehydrated polytetramethylene oxide, 1,4-butanediol, DMPA, acetone I and catalyst. After a reaction time of 1 hour at 65°C, the HDI was added and the reaction continued for another 90 min. Following the addition of acetone II, the reaction mixture had an NCO content of 0.60 %. The reaction mixture was cooled to 30°C and then mixed with the resin solution prepared from Epikote 1007 and acetone III. The mixture was then neutralized with 30 % caustic soda solution and dispersed in deionized water. The acetone was then distilled off.

## Starting materials

	Molar amount [mmol]	Parts by weight [g]
<sup>15</sup> Poly(tetramethylene oxide) (OH number = 45.0)	191	390
DMPA	239	32.1
1,4-butanediol	191	17.3
<sup>20</sup> TDI	351	61.2
HDI	351	59.1
DBTL		0.1
Acetone I		137
Acetone II		548
<sup>25</sup> Epikote 1007 (condensation polymer of bisphenol A and epichlorohydrin, $M_w$ ca 1550-2000)		240
Aceton III		240
NaOH solution (30 %)	168	22.3
<sup>30</sup> Deionized water		1200

Example 4

<sup>35</sup> The TDI was added to the mixture of dehydrated polyesterol, 1,4-butanediol, DMPA, acetone I and catalyst. After a reaction time of 1 hour at 65°C, the HDI was added and the reaction continued for another 90 min. Following the addition of acetone II, the reaction mixture had an NCO content of 0.65 %. The reaction mixture was cooled to 30°C and then mixed with the resin solution prepared from Epikote 1007 and acetone III. The mixture was then neutralized with 30 % caustic

soda solution and dispersed in deionized water. The acetone was then distilled off.

Starting materials

	Molar amount [mmol]	Parts by weight [g]
5 Polyesterdiol ADA/B14 (OH number = 45.0)	168	419
10 DMPA	235	31.5
10 1,4-butanediol	50	4.5
TDI	267	46.5
HDI	267	44.9
DBTL		0.1
Acetone I		134
15 Acetone II		534
Epikote 1007 (condensation polymer of bisphenol A and epichlorohydrin, $M_w$ ca 1550-2000)		240
Aceton III		240
20 NaOH solution (30 %)	176	23.5
Deionized water		1200

Example 5

25 The TDI was added to the mixture of dehydrated polyesterol, DMPA, 1,4-butanediol, acetone I and catalyst. After a reaction time of 1 hour at 65°C, the HDI was added and the reaction continued for another 90 min. Following the addition of acetone II, the reaction mixture had an NCO content of 0.61 %.

30 Chain-extension was carried out at 50°C by the addition of PUD, this salt being in the form of a 40 % solution in water. After 5 min, the resin solution prepared from acetone III and phenol-formaldehyde condensate was added and the mixture stirred for a further 5 min at 50°C. The mixture was then dispersed in water and 35 the acetone distilled off.

Starting materials

	Molar amount [mmol]	Parts by weight [g]
40 Polyesterdiol ADA/B14 (OH number = 45.0)	192	477

1,4-butanediol	57	5.2
DMPA	31	4.2
TDI	177	30.8
HDI	177	29.7
DBTL		0.1
Acetone I		133
Acetone II		531
PUD (40 % salt solution)	73	31.9
Phenol-formaldehyde condensate		
<sup>10</sup> $M_w$ = ca 1000-1600, softening point = 85-105°C		240
Acetone III		240
Deionized water		1200

15

Example 6

The TDI was added to the mixture of dehydrated polyesterol, 1,4-butanediol, DMPA, acetone I and catalyst. After a reaction time of 1 hour at 65°C, the HDI was added and the reaction continued for another 90 min. Following the addition of acetone II, the reaction mixture had an NCO content of 0.63 %. The reaction mixture was cooled to 30°C and then mixed with the resin solution prepared from polurethane and acetone III. The mixture was then neutralized with 30 % caustic soda solution and dispersed in deionized water. The acetone was then distilled off.

25

Starting materials

	Molar amount [mmol]	Parts by weight [g]
<sup>10</sup> Polyesterdiol ADA/B14 (OH number = 45.0)	226	564
1,4-butanediol	68	6.1
DMPA	235	31.5
TDI	305	53.1
<sup>25</sup> HDI	305	51.3
DBTL		0.1
Acetone I		173
Acetone II		690
Polyurethane (condensation <sup>40</sup> polymer of crude MDI and		

polypropylenediol, K-value in DMF at 25°C: 46)	80
Aceton III	80
NaOH solution (30 %)	176
Deionized water	1200

Example 7

10 The TDI was added to the mixture of dehydrated polyesterol, DMPA, 1,4-butanediol, acetone I and catalyst. After a reaction time of 1 hour at 65°C, the HDI was added and the reaction continued for another 90 min. Following the addition of acetone II, the reaction mixture had an NCO content of 0.45 %.

15 Chain-extension was carried out at 50°C by the addition of PUD, this salt being in the form of a 40 % solution in water. After 5 min, the resin solution prepared from acetone III and acrylate resin was added and the mixture stirred for a further 5 min at 50°C. The mixture was then dispersed in water and the acetone distilled off.

Starting materials

	Molar amount [mmol]	Parts by weight [g]
Polyesterdiol ADA/B14 (OH number = 45.0)	192	477
1,4-butanediol	57	5.2
DMPA	31	4.2
TDI	177	30.8
HDI	177	29.7
DBTL		0.1
Acetone I		133
Acetone II		531
PUD (40 % salt solution)	73	31.9
Acrylate resin comprising:		
50 wt% of <i>n</i> -butyl acrylate,		
29 wt% of ethylhexyl acrylate,		
18.5 wt% of methyl acrylate, and		
2.5 wt% of acrylic acid		240
Aceton III		240
Deionized water		1200

Example 8

The TDI was added to the mixture of dehydrated polyesterol, 1,4-butanediol, DMPA, acetone I and catalyst. After a reaction time of 1 hour at 65°C, the HDI was added and the reaction continued for another 90 min. Following the addition of acetone II, the reaction mixture had an NCO content of 0.65 %. The reaction mixture was cooled to 30°C and then mixed with the resin solution prepared from the acrylate resin and acetone III. The mixture was then neutralized with 30 % caustic soda solution and dispersed in deionized water. The acetone was then distilled off.

## Starting materials

	Molar amount [mmol]	Parts by weight [g]
15 Polyesterdiol ADA/B14 (OH number = 45.0)	168	419
DMPA	235	31.5
1,4-Butanediol	50	4.5
20 TDI	267	46.5
HDI	267	44.9
DBTL		0.1
Acetone I		134
Acetone II		534
25 Acrylate resin comprising:		
50 wt% of <i>n</i> -butyl acrylate,		
29 wt% of ethylhexyl acrylate,		
18.5 wt% of methyl acrylate, and		
2.5 wt% of acrylic acid		240
30 Aceton III		240
NaOH solution (30 %)	176	23.5
Deionized water		1200

Table

	SOLIDS CONTENT [%]	LD VALUE	VISCOSITY [mPa·s]
COMPARATIVE EXAMPLE 1	40	87	146
COMPARATIVE EXAMPLE 2	40	87	60
COMPARATIVE EXAMPLE 3	40	74	91
EXAMPLE 1	40	87	27
EXAMPLE 2	40	93	16
EXAMPLE 3	40	89	16
EXAMPLE 4	40	96	18
EXAMPLE 5	40	77	20
EXAMPLE 6	40	91	17
EXAMPLE 7	40	90	19
EXAMPLE 8	40	93	17

**We claim:**

1. An aqueous dispersion containing a polyurethane and from 5 to 60 wt%, based on the polyurethane, of a polymeric adhesion enhancer, the polyurethane being essentially built up of
  - (a) an organic polyisocyanate,  
5
  - (b) a dihydroxyl compound having a molecular weight exceeding 500 and ranging up to 5000 g/mol and not containing any anionic groups or groups capable of conversion to anionic groups,  
10
  - (c) a di- or mono-hydroxyl compound containing at least one anionic group or a group capable of conversion to an anionic group,  
15
  - (d) optionally a further compound different from (c) and containing one or two isocyanate-reactive functional groups and at least one anionic group or a group capable of conversion to an anionic group,  
20
  - (e) optionally a compound having at least two isocyanate-reactive functional groups and a molecular weight of from 60 to 500 g/mol and not containing any anionic groups or groups capable of conversion to anionic groups,  
25

and the polyurethane or its prepolymer is prepared in a water-miscible solvent boiling below 100°C and, following the addition of the polymeric adhesion enhancer, is dispersed in water and, in the case of the prepolymer, the conversion of the latter to the polyurethane is carried out.

2. A process for the preparation of an aqueous dispersion as claimed in claim 1, wherein the polyurethane or its prepolymer is formed in a water-miscible solvent boiling below 100°C and, after the addition of the polymeric adhesion enhancer, is dispersed in water and, in the case of a prepolymer, the conversion thereof to the polyurethane is carried out.  
30
3. An aqueous dispersion as claimed in claim 1, wherein the polymeric adhesion enhancer is a phenol-formaldehyde resin or an epoxide resin.  
35
4. A method of using a dispersion as claimed in claim 1 as an adhesive.

5. Substrates coated with adhesive whenever obtained by the use of a dispersion as claimed in claim 1.

**SUBSTITUTE**  
***REEMPLACEMENT***

**SECTION is not Present**

***Cette Section est Absente***